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(54) Synthesis of hydrocarbyl amines.

(57) This invention relates to a process for producing long chain alkyl amines from polyolefins by reacting

(a) a polyolefin having a molecular weight in the range of 330-2000 with ozone in the presence of a solvent,

(b) reacting the ozonolysis product from (a) without separation and/or isolation of the carbonyl compounds formed therein with a primary hydrocarbyl amines to form an imine,

(c) hydrogenation the imine from step (b) to an amine in the presence of a hydrogenation catalyst, and

(d) recovering the long chain alkyl amine from the hydrogenation products formed in step (c).

The amines so produced are useful gasoline and lube oil additives.

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SYNTHESIS OF HYDROCARBYL AMINES

This invention relates to a process for producing hydrocarbyl amines suitable for use as lube oil or gasoline activities.

Methods of producing nitrogen derivatives having long chain hydrocarbyl chains are well known. For instance GB-A-1172818 (Monsanto) describes a process for producing Schiff's bases by oxidising a polyolefin with ozone in the presence of an alcohol followed by conversion of the oxidation product to a carbonyl compound and reaction of the carbonyl compound after separation thereof from the ozonolysis products with an amine results in a Schiffs base.

This necessary separation and/or purification of the carbonyl compound from the ozonolysis products prior to reaction with an amine would appear to make the process commercially non-viable.

An alternative method is that described in EP-A-244616 (BASF AG) where a polybutene is subjected to a hydroformylation reaction and the resultant mixture of oxo products is subjected to either (a) a Mannich reaction or (b) a hydroamination reaction.

This reaction has the disadvantage that the hydroformylation product has a mixture of long chain aldehydes, ketones and long chain alcohols. Such a mixture of products, especially the presence of long chain alcohols, which are not separated prior to the Mannich reaction or hydroamination, give a complicated mixture of products.

Moreover, the long chain alcohols may have a detrimental effect on the aminated end product when used eg. as lube oil additives or gasoline additives.

It has now been found that the problems associated with such prior art process can be mitigated by (a) avoiding the separation steps of the GB-A-1172818 and also the hydroformylation step of E-A-244616.

Accordingly, the present invention is a process for producing long chain alkyl amines from polyolefins, said process comprising reacting

(a) a polyolefin having a molecular weight in the range of 330-2000 with ozone in the presence of a solvent,

(b) reacting the ozonolysis product from (a) without separation and/or isolation of the carbonyl compounds formed therein with a primary hydrocarbyl amines to form an imine,

(c) hydrogenating the imine from step (b) to an amine in the presence of a hydrogenation catalyst, and

(d) recovering the long chain alkyl amine from the hydrogenation products formed in step (c).

The polyolefin which is ozonolysed is suitably a polymer of a C_2-C_4 olefin or a copolymer thereof and has a molecular weight in the region of 330-2000, preferably from 500 to 1500. Of these, polybutenes, especially those containing significant proportions of polyisobutene i.e. Hyvis, Napvis and Ultravis (all Registered Trade Marks, ex BP Chemicals) are preferred.

The ozonolysis of the polyolefin in step (a) above is suitably carried out by bubbling ozone in the gaseous phase, with or without an additional diluent, through a solution of the polyolefin in a solvent. Examples of solvents that may be used include alcohols and hydrocarbons, preferably aliphatic, straight chain alcohols which have 1-12 carbon atoms in the chain. In the case of alcohols, these preferably have 1-4 carbon atoms in the chain.

The ozonolysis temperature is suitably from -70 to +50°C, preferably -30 to +30°C and most preferably from -10 to +30°C. The reaction is exothermic and hence care should be taken to ensure that the reaction temperature does not exceed 50°C, if necessary by cooling.

The solvent is suitably present in the reaction mixture in a weight ratio of 1:1 to 10:1 with respect to the polyolefin polyolefin reactant.

For this reaction it is essential to ensure that the proportion of ozone to olefin reacted at a given temperature and pressure are such that no explosive mixtures are formed. The explosive limits for the various reaction conditions are well known to those skilled in the art.

The ozonolysis products from step (a) are contacted with a primary amine in step (b). For this step the ozonolysis products are used directly, i.e. without any prior separation step, for reaction with the primary amine. Prior to contact of the ozonolysis products with the primary amine, it is preferable to (i) remove any excess ozone therein by sparging an inert gas eg. nitrogen therethrough and (ii) to wash the ozonolysis products with water in order to remove any lower boiling fractions such as eg. acetone.

The primary hydrocarbyl amines used to react with the ozonolysis product may be one or more of mono- di- and polyamines which may be aliphatic, alicyclic or aromatic in nature.

Typical examples of amines which can be used in preparing compounds of this invention are diethylenetriamine, di(methylethylene)triamine, triethylenetetramine, tri(methylethylene)tetramine, tri(ethylethylene)tetramine, tetraethylenepentamine, pentaethylenehexamine, ethylenediamine, hexamethylenediamine, o - phenylenediamine, m-

phenylenediamine, p -phenylenediamine, alkyl-substituted o-, m- and p - phenylenediamine, dimethylaminomethylamine, dimethylaminoethylamine, dimethylaminopropylamine, dimethylaminobutylamine, dimethylaminoheptylamine, diethylaminomethylamine, diethylaminopropylamine, diethylaminoamylamine, dipropylaminopropylamine, methylpropylaminoamylamine, propylbutylaminoethylamine, dimethylenetrianilinemethylenedianiline, polymethyleneaniline and polyalkylmethyleneaniline.

The reaction of the ozonolysis product from step (a) with the primary amine in step (b) is suitably caried out at a temperature in the range of e.g. 50-200 °C. This reaction with primary amine is carried out by continuous removal of water formed during the reaction reaction along with any incidental volatilization of solvents already present in the reaction mixture.

In this reaction the molar ratio of the ozonolysis products to the primary amine is suitably from 1:1 to 1000:1, preferably from 1:1 to 5:1.

The product of the reaction in step (b) is a hydrocarbyl imine. Also present in this product are water and solvents specially those used for step (a) above.

The water and solvents are separated from the imine product by eg. filtration and/or fractional distillation.

The separated imine product from step (b) is then hydrogenated to form the desired amine.

The hydrogeneration of the imine may be carried out under homogeneous on heterogeneous conditions.

The hydrogenation is carried out using catalyst such as Raney nickel, palladium or carbon, palladium on silica and the like.

The hydrogenation reaction is suitably carried out a pressure of up to 20 MPa, preferably from up to 10 MPa, more preferably from up to 8 MPa.

The hydrogenation reaction is suitably carried out at a temperature from 0 to 200 °C, preferably from 50 to 150 °C.

Where the hydrogenation reaction is carried out under heterogeneous conditions, the removal of catalyst residues is facilitated. For this purpose, solvent extraction of the amine product can be used. The preferred solvents are aliphatic alcohols or hydrocarbons.

The desired amine can thus be recovered from the reaction products of hydrogenation by filtering off the catalyst and removing the solvent from the filtrate by distillation.

The hydrocarbyl amines of the present invention can be used as lube oil additives, fuel additives and as gasoline detergents.

The present invention is further illustrated with reference to the following Examples.

Examples

A. Production Imines

1. In a tubular glass vessel equipped with a gas disperser at its base and an isothermal jacket was placed 100g of a polyisobutene (NAPVIS 10, RTM) of M-n-1000 and 100ml of n-hexane. Ozone was then passed through the polyisobutene solvent mixture at 15 °C at the rate of 0.13 moles per hour. After four hours the ozone supply was stopped and nitrogen was passed through the reaction mixture for a short time (2 minutes) to remove any unreacted ozone in the vessel which now contained the ozonolysis products. 0.2 moles of dimethylaminopropylamine was then added to the ozonolysis products whilst the passage of nitrogen was continued for a further 2 minutes. The contents of the vessel were then transferred to a glass reactor (500ml capacity) equipped with a condenser. The contents of the reactor were refluxed (71 °C) for 2 hours and finally the reaction mixture evaporated in a rotary evaporator under vacuum at 140 °C using an oil bath. The non-volatile residue remaining after evaporation was the imine intermediate which was yellow and contained 1.8%w/w nitrogen 115g of product was recovered with an imine yield of approximately 64% molar.

2. In a tubular glass reactor, which was about five times larger in diameter than the used in A(1) above, was placed 650g of a polyisobutene of M_n 1000 and a mixture of n-hexane and methanol (300ml each). Ozone containing small quantities of air was passed through the polyisobutene/solvent mixture with vigorous stirring. During this operation further aliquots of a 50/50wt% mixture of n-hexane and methanol (total 300ml) was added from time to time. The reaction proceeded for 6.5 hours. The ozone supply was thereafter stopped and the reaction mixture sparged with nitrogen to remove any unreacted ozone therein. Thereafter water (300ml) was added to the reaction mixture. The whole contents of the reactor were then transferred to another vessel and the aqueous phase allowed to separate. This happened readily and the aqueous layer was removed.

220g of the non-purified organic product was mixed with 800ml of toluene and 24.74g of commercial tetraethylene pentamine in 200ml of toluene. The whole mixture was heated to boiling and 400ml of solvent removed after 4 hours. The remaining solvent was removed in a rotary evaporator under oil pump vacuum at 140 °C.

240g of product was recovered from the evaporator and contained 3.1% w/w nitrogen corresponding to an imine yield of approximately 66% molar.

A comparison of the above A(1) and A(2) process shows that much less ozone is needed in a stirred reactor than in a non-stirred reactor for similar imine yields.

Hydrogenation of Imine

70g of the imine product from procedure A(1) above was placed in a high pressure autoclave (300ml) capacity equipped with a mechanical stirrer together with a 80ml of cyclohexane. 5g of a freshly ethanol-washed commercial sample of Raney nickel together with 20ml ethanol was also added to the autoclave which was then sealed and degassed with hydrogen. The contents of the autoclave were vigorously stirred under a hydrogen atmosphere for 15Mpa and maintained at 90°C for 19 hours. The stirring was stopped and the contents of the autoclave allowed to cool and subsequently depressurised. The reaction mixture was filtered and the filtrate evaporated on a rotary evaporator as in A(1) above. The resultant straw coloured residue showed negligible adsorption in the infrared spectral region of $1800cm^{-1}$ and $1600cm^{-1}$ signifying the absence of any imine or carbonyl functions in the product. The product had a nitrogen content of 1%w/w.

Claims

1. A process for producing long chain alkyl amines from polyolefins, said process comprising reacting

(a) a polyolefin having a molecular weight in the range of 330-2000 with ozone in the presence of a solvent,

(b) reacting the ozonolysis product from (a) without separation and/or isolation of the carbonyl compounds formed therein with a primary hydrocarbyl amines to form an imine,

(c) hydrogenating the imine from step (b) to an amine in the presence of a hydrogenation catalyst, and

(d) recovering the long chain alkyl amine from the hydrogenation products formed in step (c).

2. A process according to claim 1 wherein the polyolefin which is ozonolysed is a polymer of a C_2-C_4 olefin or a copolymer thereof and has a molecular weight in the region of 330-2000.

3. A process according to any one of the preceding claims wherein the ozonolysis of the polyolefin in step (a) above is carried out by bubbling ozone in the gaseous phase, with or without an additional diluent, through a solution of the polyolefin in a solvent.

4. A process according to any one of the preceding claims wherein the ozonolysis temperature is from -70 to +50°C.

5. A process according to any one of the preceding claims wherein the primary hydrocarbyl amines used to react with the ozonolysis product is selected from one or more of mono- di- and polyamines which may be aliphatic, alicyclic or aromatic in nature.

6. A process according to any one of the preceding claims wherein the reaction of the ozonolysis product from step (a) with the primary amine in step (b) is carried out at a temperature from 50-200°C.

7. A process according to any one of the preceding claims wherein in the reaction of the ozonolysis products with the primary amine, the respective molar ratios of the two is from 1:1 to 1000:1.

8. A process according to any one of the preceding claims wherein the hydrogenation of the imine from step (c) is carried out using catalyst such as Raney nickel, palladium on carbon or palladium on silica.

9. A process according to any one of the preceding claims wherein the hyrogenation reaction is carried out a pressure of up to 20 MPa.

10. A process accoridng to any one of the preceding claims wherein the hydrogenation reaction is carried out at a temperature from 0 to 200°C.

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EUROPEAN SEARCH REPORT

Application Number

EP 89 40 0383

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,A	EP-A-0 244 616 (BASF) * Claims * ---	1-10	C 07 C 209/26 // C 10 M 133/54
D,A	GB-A-1 172 818 (MONSANTO) * Whole document * -----	1-10	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 07 C 209/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	06-10-1989	HELPS I.M.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document